THE TREND OF PHOSPHATE ADSORPTION BY INORGANIC COLLOIDS FROM CERTAIN INDIANA SOILS

BY

LOWELL EDWARD ALLISON

B. S., Purdue University, 1930

M. S., University of Illinois, 1933

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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INTRODUCTION

Most arable lands are deficient in the essential element phosphorus and therefore its applications in a readily available form has become a fundamental soil management practice. Since the colloidal fraction of the soil has the inherent property of rapidly rendering applied soluble phosphates, such as superphosphate, insoluble and therefore unavailable the manner of its application is of extreme importance in farm economy. Extensive field researches on this problem have indicated the practice of localized application of soluble phosphates as a means of giving the plants a greater option on the phosphate than it does the fixing agencies of the soil. Recognition of the fact that soils fix phosphates in difficultly available forms does not imply an understanding of the nature of the forces responsible for such fixation. Because of the overlapping effect of many of these forces it is often difficult, if not impossible, to properly evaluate the role of each independent force in a system so complex as the soil.

HISTORICAL

The literature on phosphate fixation indicates two general types of reactions, i.e., fixation by precipitation and fixation by adsorption. Precipitation of phosphates by Ca chiefly, as the tri-calcium salt occurs in soils when the reaction exceeds pH 6.5 In calcareous alkaline soils the formation of high calcium salts such as carbonate-apatite ($3\ Ca_3(PO_4)_2 \cdot CaCO_3$) and hydroxy-apatite ($3\ Ca_3(PO_4)_2 \cdot Ca(OH)_2$) is regarded as a contributing factor to low phosphate availability.

The early literature is rich in references to the formation of insoluble phosphates of Fe and Al in acid soils not dominated by Ca, with the implication that these ions are alone responsible for such action. Except in strongly acid soils the quantity of ionic Fe and Al is considered to be too low to account for any considerable precipitation of phosphate.

More recently attention has been focused on the adsorption of phosphate anions by hydrated oxides (hydrogels) of iron and to some extent aluminum, which are considered active in this respect. This is illustrated by the following equation:

$$Fe_2O_3 \cdot H_2O + H_3PO_4 = Fe_2(OH)_3PO_4 + H_2O$$
(Goethite) (Dufrenite)

Because artificially prepared Fe and Al hydrogels have been shown to adsorb phosphate anions tenaciously, the natural soil hydrogels of these elements are considered to be more important in rendering phosphates insoluble by adsorption than are the ions of Fe and Al by precipitation.

Within the last decade the role of alumino-silicate colloids in rendering phosphates insoluble has received considerable attention. Scarseth (2) found that bentonite (montmorillonite) adsorbed phosphate anions in significant quantities within the pH range of 5.0 to 7.0 with a maximum adsorption at pH 6.0. Stout (3) observed that kaolinite and halloysite adsorbed exceedingly large amounts of phosphate at pH 3.0 to 4.0 with a progressive decrease in this property with increase in pH.

In soils containing exchangeable Ca, phosphorus may be retained by a phenomenon referred to as "saloid-bound". By this type of linkage the phosphorus, probably as the $H_2PO_4^-$ anion, is loosely held to the micelle by the calcium ion, which shares its valences between the micelle and the phosphate anion. Because of the instability of this linkage phosphorus so held is regarded as readily available to plants.

The present investigation was undertaken to obtain more fundamental information on the trend of phosphate adsorption by the inorganic colloids isolated from certain Indiana soils of widely varying character. Attention was also given to the merits of the practice of removing superficial iron oxide from soil colloids for studies of this nature, including a comparison of a well known chemical method and a recently devised biological method for this purpose.

EXPERIMENTAL METHODS

For this study the Miami and Cincinnati silt loams were selected as representing a youthful and an advanced stage of

maturity respectively from glacial drift. A Frederick silt loam, residual from cherty limestone, was also included to represent the most advanced stage of soil maturity in Indiana.

The inorganic colloids of less than one micron in effective diameter were isolated from the B horizon from each of these soils by a sedimentation procedure. Each colloid was divided into two portions one of which was electrodialyzed to remove all mobile ions. The other portion was first treated to remove free iron oxides by a biological method (1), after which it was treated with H_2O_2 to remove organic matter and subsequently electrodialyzed. The chemical method of Truog (4) was used for comparison on the Miami colloid.

Phosphate adsorption experiments were conducted on the treated and untreated colloids by the technique described by Scarseth (2). As used in this investigation it involved the addition of three concentrations of H_3PO_4 to fixed amounts (1 gm) of the colloids in 100 ml volume of suspension with variations in reaction over the pH range 3.0 to 8.0 by additions of either NaOH or $Ca(OH)_2$. After an equilibrium period of 5 days at 24-26° C, clear extracts, obtained by centrifuging, were analyzed for phosphorus by a colorimetric method. The amount of phosphate adsorbed was determined by subtracting the amount in solution from that added and reported in millimoles adsorbed per 100 gm of colloid.

RESULTS AND SUMMARY

The data from the several phosphate adsorption experiments are expressed graphically in the curves shown in Figure 1. The concentrations of H_3PO_4 are represented by the numbers 5, 15 and 30 which represent millimoles of this acid used per 100 gm of colloid.

The results of this investigation may be summarized as follows:

1. A biological method for removing free iron oxides from colloidal clays was compared with the chemical method of Truog for this purpose. Based on the amount of iron oxide removed from the Miami colloid the biological method is as effective as the chemical method for this purpose.

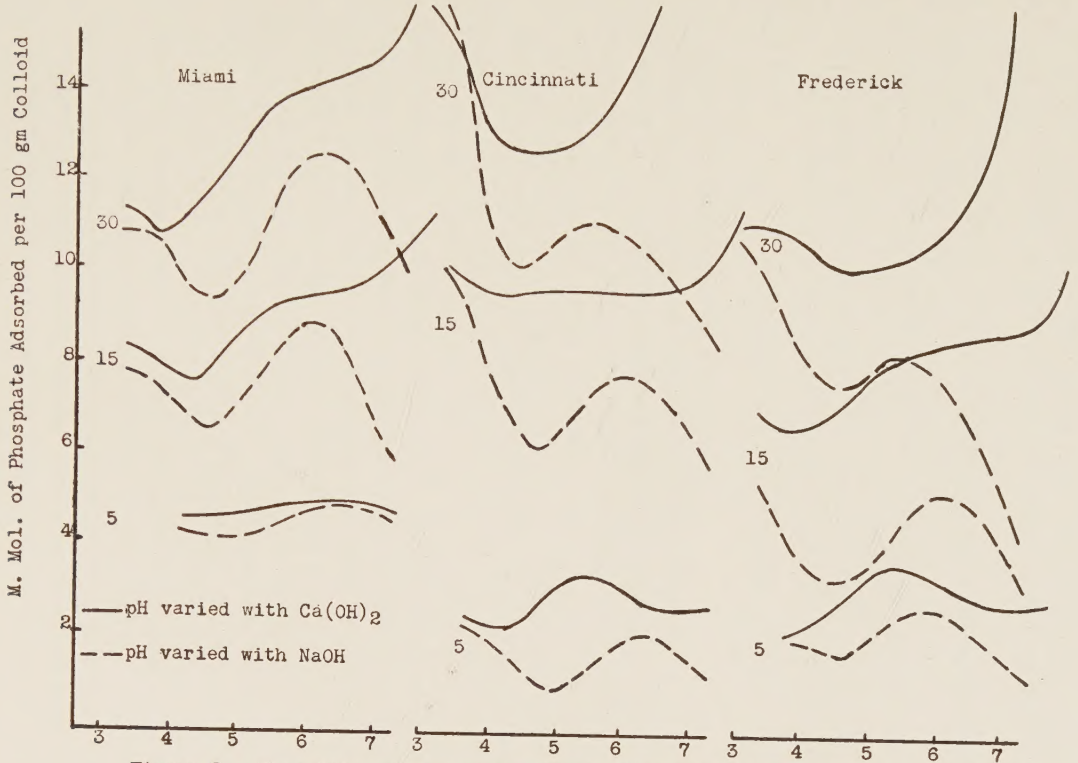

Figure 1. Phosphate adsorption by Miami, Cincinnati and Frederick colloids at three levels of phosphate and in the presence of calcium and sodium cations.

2. Attempts to establish the phosphate adsorption behavior at pH 3.0 to 5.0 of alumino-silicate minerals present in soil colloids by first removing free oxides of iron were unsuccessful. Apparently forms of iron, and perhaps other constituents not removed by extraction methods, were responsible for the observed high phosphate adsorption by the treated (gray) colloids within the low pH range. In view of these results the practice of removing free iron oxides from soil colloids in preparation for phosphate adsorption studies is of little merit.

3. Where sodium was the exchangeable cation, the curves of phosphate adsorption over the pH range 3.0 to 8.0 by the Miami, Cincinnati and Frederick colloids indicate a characteristic "maximum" and "minimum" effect. The first peak of adsorption occurs at pH 3.0-3.5 and is believed to be due mainly to the hydrated forms of iron and to a less extent aluminum associated with the colloid. A second agency, active over the pH range 5.5 to 6.5, adsorbs a maximum of phosphate at approximately pH 6.0. This is thought to be due to alumino-silicate adsorption of phosphate by anion exchange. Between the two adsorption maxima at pH 3.0 and 6.0 respectively, a much lower adsorption occurs at pH 4.5, apparently due in part to each of the above mentioned types of reactions.

4. Where calcium was the exchangeable cation the phosphate retention was appreciably greater than in the presence of sodium. This is indicated by the relatively higher position of the calcium curves in Figure 1 over those of sodium. The divergence in the two curves appears to be moderately uniform over the pH range 4.5 to 6.0 which indicates that in acid soils exchangeable calcium is probably an important factor in retaining phosphorus in the most readily available of all of its fixed forms, i.e., in the $H_2PO_4^-$-Ca-Micelle linkage.

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VITA

The author was born September 19, 1904, near Stryker, Ohio. He attended a rural elementary school for eight years and graduated from Stryker High School in 1923. Three years later he enrolled in Purdue University, graduating in 1930. The next seven years were spent in graduate study and research in Agronomy at the University of Illinois during which period the M.S. degree was granted. On January 1, 1937, he assumed appointment as Instructor in Soils at Purdue University, a position he now holds with the rank of Assistant Professor.

The author is a member of Sigma Xi, honorary scientific fraternity; Gamma Sigma Delta, and Alpha Zeta, honorary fraternities in agriculture, and Ceres, a local fraternity in Agronomy at Purdue University.